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Secular variations in atmospheric O2 level during and after the Paleoproterozoic Snowball Earth Glaciation

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The early Paleoproterozoic was a pivotal interval in the development of Earth's habitability, characterized by widespread glaciations, some of which may have reached Snowball Earth conditions, and by the Great Oxidation Event (GOE). A long-standing hypothesis links the severe early Paleoproterozoic glaciations to the GOE via oxidation-driven collapse of atmospheric CH_4. However, the GOE, defined by the permanent loss of mass-independent sulfur isotope fractionation (S-MIF), postdates the onset of these glaciations, challenging a simple causal relationship. Moreover, growing evidence suggests the GOE was not monotonic but episodic, with multiple intervals of S-MIF disappearance and reappearance, further complicating glaciation–oxygenation linkages.

The Makganyene Formation, a benchmark glacial diamictite deposited in the Griqualand West sub-basin of the Transvaal Supergroup on the western Kaapvaal Craton, South Africa, is interpreted as a Snowball Earth glaciation based on paleomagnetic constraints. Here, we investigate the stratigraphic transition from the Makganyene Formation into the overlying Hotazel and Mooidraai formations using multiple drill cores. Guided by detailed petrofacies analysis, we quantify pyrite trace-element systematics (EPMA) and triple sulfur isotopes ($\delta^{34}S$, $\Delta^{33}S$; NanoSIMS) across distinct pyrite populations, and assess carbonate-associated rare earth element (REE) patterns.

Makganyene diamictites contain abundant detrital pyrite, consistent with glacial reworking, whereas detrital pyrite is absent from the Hotazel and Mooidraai strata. Early diagenetic pyrite, distinguished by morphology and trace-element signatures, occurs throughout the succession. Makganyene pyrites exhibit pronounced S-MIF ($|\Delta^{33}S| > 1‰$), whereas Hotazel pyrites lack S-MIF, implying near-anoxic conditions during Makganyene deposition ($<10^{-5}$ PAL) followed by a major oxidation episode during Hotazel time. This interpretation is independently supported by strong negative Ce anomalies in Hotazel carbonates (Ce/Ce* down to 0.27). Notably, some Mooidraai pyrites return significant S-MIF ($|\Delta^{33}S| \sim 1‰$), indicating a subsequent decline in atmospheric O_2, consistent with the absence of negative Ce anomalies in this interval.

Overall, our results suggest that Paleoproterozoic Snowball Earth glaciation coincided with—and may have modulated—large-amplitude, dynamic changes in surface redox state across the atmosphere and upper ocean, with important implications for early biogeochemical cycling and life.

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